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van Loosdrecht, P. H. M. ; Boucher, J. P.; Martinez, G.; Dhalenne, G.; Revcolevschi, A.

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Magnetic fluctuation spectrum of $CuGeO_3$: Raman scattering

P. H. M. van Loosdrecht, J. P. Boucher, and G. Martinez
Grenoble High Magnetic Field Laboratory, Max-Planck-Institut für Festkörperforschung and Centre National de la Recherche Scientifique, 25 Avenue des Martyrs, BP 166, F-38042 Grenoble Cedex 9, France

G. Dhalenne and A. Revcolevschi
Laboratoire de Chimie des Solides, Univerité de Paris-Sud, bâtiment 414, F-91405 Orsay, France

Raman spectra of the magnetic fluctuation spectrum of $CuGeO_3$ are presented for $4<T<300$ K and $B\leqslant 20$ T. For $B=0$ the results show good agreement with theoretical expectations for a one-dimensional isotropic Heisenberg antiferromagnet which exhibits a spin–Peierls transition. In the presence of a magnetic field the phase transition to the incommensurately modulated phase is observed around $B=12.8$ T at $T=4.2$ K. The spectra obtained in the high field phase clearly show evidence for a well-defined spin fluctuation spectrum, which appears to present an intermediate case between the dimerized phase and the short-range order regime of the uniform phase. © *1996 American Institute of Physics.* [S0021-8979(96)73108-8]

I. INTRODUCTION

Recently it has been shown that $CuGeO_3$, an inorganic compound, undergoes a spin–Peierls distortion below 14 K.[1] The magnetic interactions above this second-order transition are well described as a nearly one-dimensional isotropic $S=1/2$ Heisenberg antiferromagnet. The magnetic fluctuations in such a quantum system are of special interest due to the lack of long-range order, and differ substantially from what one expects for a classical system. In the dimerized (D) phase, one expects a gap in the fluctuation spectrum. The occurrence of this gap in $CuGeO_3$ has been confirmed by various experimental techniques.[2–4] Applying a magnetic field in the D phase induces a second phase transition, of first order, to a presumably incommensurate (IC) phase around $B=13$ T.[3,5]

$CuGeO_3$ has an orthorhombic structure with a space group $Pbmm$.[6] The magnetic chains are formed by the $S=1/2$ Cu^{2+} ions running along the c axis of the crystal. The magnetic interaction is described by the isotropic Heisenberg Hamiltonian $H=\Sigma_i 2J_i \mathbf{S}_i\mathbf{S}_{i+1}$, with an intrachain exchange coupling $J=J_c\approx 60$ K. In the dimerized phase small interchain couplings $J_b\approx 0.1J_c$ and $J_a\approx -0.01J_c$ have been found.[2]

The present article is concerned with the magnetic fluctuation spectrum of $CuGeO_3$ in the uniform (U), the D, and the IC phase as probed by polarized Raman scattering experiments. Generally the most important contribution to magnetic inelastic scattering in antiferromagnets is the exchange scattering mechanism. In $CuGeO_3$ the scattered intensity can be expressed as $I(\omega)\propto\Sigma_{\mathbf{q}} f_{\mathbf{q}}\langle S^{\alpha}_{\mathbf{q}}(t)S^{\alpha}_{-\mathbf{q}}(t) \times S^{\alpha}_{\mathbf{q}}(0)S^{\alpha}_{-\mathbf{q}}(0)\rangle_{\omega}$, where $f_{\mathbf{q}}=\cos^2(q_c)$ is the weighing function which arises from the matrix elements for the exchange interaction.[7] The magnetic scattering is thus mainly due to the density of states (DOS), and the structure therein, in the first-half of the Brillouin zone.

II. EXPERIMENT

The samples used in this study were grown from the melt by a floating zone technique.[8] They were cleaved perpendicular to the (100) direction and mounted in a cold finger flow cryostat (temperature accuracy ~1 K). Raman spectra have been recorded in a backscattering geometry using a charge-coupled device equipped spectrometer (DILOR XY). The 514 nm line of an Ar-ion laser was used for excitation, keeping the intensity below 200 W/cm^2 to minimize local heating. Polarized experiments have been performed in a $(\mu\nu)$ scattering geometry, where μ,ν denote the polarization of the incident and scattered light, respectively. Magnetic scattering is only observed in the (cc) geometry, where c is along the chain direction. The results obtained in other geometries, as well as the results on vibrational scattering and wavelength dependence will be presented elsewhere.[9]

III. RESULTS FOR $B=0$ T

The magnetic scattering in $CuGeO_3$ is found to be strongly temperature dependent. As shown in Fig. 1, three types of behavior can be distinguished. In the uniform phase a well-defined broad scattering band is observed centered around 230 cm^{-1} for temperatures below 60 K [Fig. 1(b)]. This is also the temperature where the maximum in the susceptibility curve is observed. Above this temperature the scattered intensity is observed to be transferred to a quasielastic central peak which gains intensity as the temperature increases [Fig. 1(c)]. In the D phase [$T<14$ K, Fig. 1(a)], the broad maximum becomes sharp, and several new, sharp features appear in the spectrum at 32, 105, 370, and 820 cm^{-1}.

A detailed discussion of the results obtained for $B=0$ has been given elsewhere.[7] Here only the key points are discussed. The observed spectra in the U phase can be understood in terms of the magnetic fluctuation spectrum expected for a one-dimensional $S=1/2$ Heisenberg antiferromagnet.[10] Although such a system does not order, not even at $T=0$, short-range correlations do develop at low temperatures. In this short-range order (SRO) regime the fluctuation spectrum is expected to form a continuum in $(\omega,\mathbf{q})$ space, bounded by $\omega_1(q_c)=\pi J|\sin(q_c)|$ and $\omega_2(q_c)=2\pi J|\sin(q_c/2)|$. The intensity of the fluctuations in this spin wave continuum (SWC) diverges at the lower limit $\omega_1(q_c)$, and rapidly decreases for increasing frequency. Using this description one can now understand the observed spectrum in the SRO regime [Fig. 1(b)]. The maximum in intensity around 230 cm^{-1} arises due

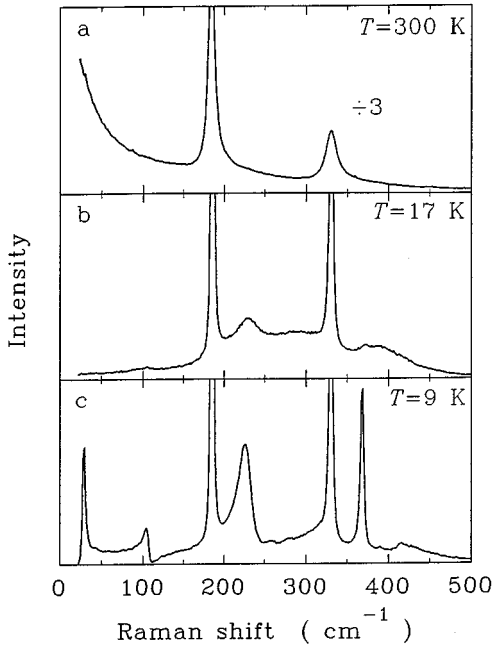

FIG. 1. Polarized (cc) Raman spectra of $CuGeO_3$ in the uniform and dimerized phases. (a) Uniform phase, high temperature regime. (b) Uniform phase, short-range order regime. (c) Dimerized phase. Spectrum (a) has been scaled down by a factor of 3.

to fluctuations around $q_c=\pi/2$, where the flatness of $\omega_1(q_c)$ yields a strongly peaked DOS. Model calculations including only the SWC show a good agreement with the observed spectrum for $\omega<250$ cm^{-1}, using $J=60$ K. The intensity at higher energies, however, cannot be due to the SWC. The origin of this high energy scattering is not fully understood at present, but preliminary results on the pressure dependence of the spectrum indicate that it is due to spin–phonon interactions.[9]

As the temperature increases the magnetic correlation length becomes shorter and the above picture breaks down. In the absence of correlations the magnetic fluctuations become diffusive, and the intensity of the fluctuation spectrum is transferred toward $(\omega,\mathbf{q})=(0,\mathbf{0})$. Since the magnetic system of $CuGeO_3$ is nearly one dimensional this leads to a divergent DOS at $\omega=0$. The Raman spectrum at high temperatures [$T>60$ K, Fig. 1(a)] indeed shows a quasidiverging central peak with a tail extending up to 400 cm^{-1}.

The magnetic fluctuation spectrum in the D phase [Fig. 1(c)] shows two peaks which can be assigned to two-spin scattering processes. The first peak at 32 cm^{-1} is due to the spin–Peierls gap at $(q_b,q_c)=(0,\pi)$, and shifts to lower frequency as the temperature approaches the spin–Peierls transition. The peak around 230 cm^{-1} is due to the maximum in the DOS for $q_c=\pi/2$. In addition to this purely magnetic scattering there are several other peaks observed in the D phase, which disappear in the U phase. The asymmetric peak at 105 cm^{-1} could be due to the gap in the fluctuation spectrum at $(q_b,q_c)=(0,0)$. However, the position of the peak is independent of temperature and no splitting of this peak has been observed in a magnetic field. Therefore this peak cannot be due to a spin–Peierls gap. It is more likely that this peak

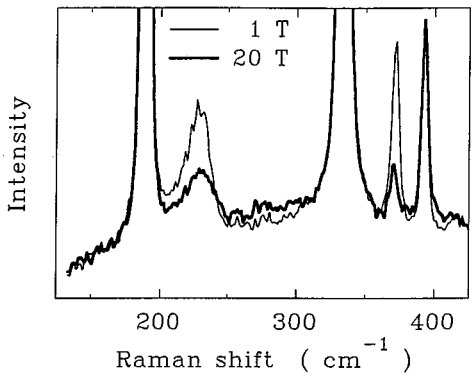

FIG. 2. Unpolarized Raman spectra of $CuGeO_3$ in the D and IC phase at $T=4.2$ K. (a) D phase, $B=1$ T, (b) IC phase, $B=20$ T.

is in fact due to a phonon which is activated by the cell doubling in the D phase, where its asymmetry is due to a coupling to the spin system. Also the peak at 370 cm^{-1} cannot be due to purely magnetic excitations, given its relatively high energy, and again the cell doubling in the D phase may be responsible for the appearance of this peak in the Raman spectrum.

IV. RESULTS FOR $B\neq 0$ T

Figure 2 shows representative unpolarized Raman spectra for the D phase ($B=1$ T) and the IC phase ($B=20$ T) at $T=4.2$ K. In order to clarify the magnetic contribution, the B_{1g} phonon at 228 cm^{-1} has been suppressed by subtracting the same Lorentzian peak from both spectra. It is interesting to compare the spectrum observed in the IC phase to those obtained in the D phase and in the SRO regime, since the spectrum observed in the IC phase appears to present an intermediate case between those in the D phase and in the SRO regime. It is clear that, like in the SRO regime, in the

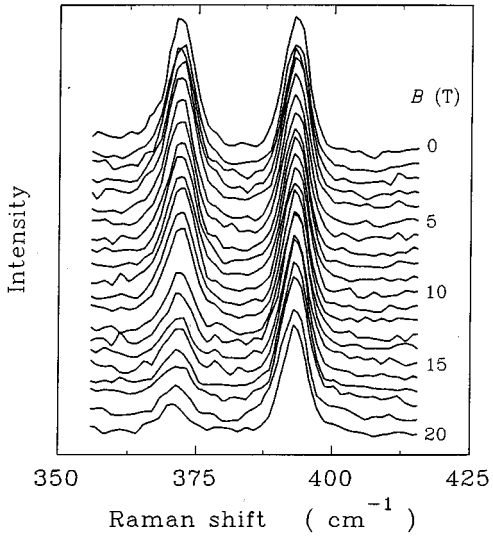

FIG. 3. Field dependence of the 370 cm^{-1} mode showing the discontinuous decrease at the D–IC phase transition around 12.8 T. The mode at 394 cm^{-1} is assigned to a B_{1g} phonon.

IC phase the maximum around 230 cm^{-1} broadens and loses some intensity as compared to the D phase, but the changes are found to be less drastic. Also the increase in intensity for energies above 230 cm^{-1} found in the SRO regime is observed in the IC phase, but again is less pronounced. Hence, many of the characteristics of the D phase are retained in the IC phase. This also holds for the mode observed at 370 cm^{-1} in the D phase, which is absent in the SRO regime. In fact the intensity of this mode provides a convenient means to study the phase transitions in $CuGeO_3$. Upon increasing the temperature from either the IC or the D phase the intensity of this mode continuously decreases until it has completely disappeared at the second-order phase transition to the U phase. The magnetic field dependence at 4.2 K of this mode is shown in Fig. 3, which also shows the B_{1g} phonon at 390 cm^{-1}. This phonon structure is found to be field independent, and is used as a reference for comparison to the 370 cm^{-1} feature. Upon increasing magnetic field, starting from the D phase the intensity of the 370 cm^{-1} mode slowly decreases. At the first-order D–IC phase transition the intensity drops sharply by about 20% over 0.2 T, after which it continues to decrease slowly until it reaches a more or less stable value around 17 T. Clearly this mode is intrinsic not only to the D phase, but also to the IC phase.

The observation that the Raman spectra in the IC phase shows characteristics of both the D phase and the SRO regime might not be so surprising since one can anticipate that the *average* structure of the high field phase is the same as the structure of the U phase, whereas the *actual* structure is likely to be close to the dimerized structure of the D phase. In other words, it seems likely that the D phase is the lock-in phase of the IC phase, which itself is obtained by an incommensurate modulation of the U phase with a modulation wave vector close to 1/2 (the commensurate modulation of the D phase). Whether this picture holds, however, remains to be proven and has to await theoretical results for the IC phase which are not available at present.

V. CONCLUSIONS

The results obtained on the fluctuation spectrum of $CuGeO_3$ in the U phase clearly show the importance of quantum spin fluctuations in this system. In the first place the observed maximum around 230 cm^{-1} can only be understood from a quantum description, classically this energy is scaled down by a factor $\pi/2$. In the second place, the spectrum in the SRO regime of the U phase has no classical interpretation and is due to SWC excitations. In the third place the observed diffusive scattering at low energies which start to develop already at low temperatures, and dominates the high temperature spectra is in good agreement with the $T>0$ finite quantum spin chain calculations of Müller *et al.*[10]

The results obtained in the IC phase clearly show the existence of a continuum of spin excitations, whose spectrum appears to present an intermediate spectrum between the D phase and the SRO regime of the U phase.

It is clear from the discussions in the present article that many aspects of the spin fluctuation spectrum are only qualitatively understood. This is mainly due to the lack of theoretical results for B and/or $T\neq 0$ for this magnetoelastic compound. We hope therefore that the present results stimulate further theoretical and experimental work on this fascinating system.

ACKNOWLEDGMENT

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